

REMARKS

The Office Action of July 5, 2005 presents the examination of claims 36, 39 and 41-52. Claims 39 and 41-52 are allowed.

Claim 36 stands rejected under 35 USC § 103(a) as being unpatentable over Sato et al. JP '977 in view of Pohl et al. '233, Williams et al. '080 and Beratan et al. '063 (and IBM Technical Disclosure Bulletin). This rejection is respectfully traversed. Reconsideration and withdrawal thereof are requested.

Applicants submit that the Examiner fails to establish a proper case of *prima facie* obviousness of the invention described in claim 36. In particular, the Examiner does not explain the motivation that urges the artisan of ordinary skill to combine the references as the Examiner has done. Such explanation of motivation is a requirement of a proper case of *prima facie* obviousness; this requirement is to prevent the imposition of rejections based upon improper hindsight reconstruction of the invention using the present claim and specification as a template upon which to assemble the elements of the invention taken individually from the prior art. The mere fact that the prior art can be modified is not sufficient; there must be an explanation provided by the prior art as to why the modification is desirable. *See, In re Fritch*, 23 USPQ2d 1780 (Fed. Cir. 1992).

Applicants submit that improper hindsight reconstruction of the invention is exactly what the Examiner has indulged in to make the instant rejection.

The primary reference Sato is characterized by the Examiner as describing photoreduction of a viologen salt by a polyvinyl alcohol, providing a photochromic effect. Sato does not at all describe any sort of a conductive polymer being formed. The Examiner is confusing an oxidation of the polyvinyl alcohol (chemical transfer of an electron from the PVA) with a conductive state (mobility of electrons down a voltage gradient). The main objective of Sato is to obtain a composition which exhibits high photosensitivity and film forming activity.

Further information of how PVA participates in the photoreduction of viologen can be obtained from the reference attached (Ogawa et al), which describes the change in color of methyl viologen when it is reduced by absorption of an electron generated by oxidation of PVA by gamma radiation or electron beam radiation (as a model of beta rays). Like Sato, Ogawa et al also do not provide any evidence that any electrical conductivity achieved. In fact, it is highly unlikely, if not impossible for PVA, a non-conjugated polymer, to allow the transport of electrons along its chains. It is certainly not the case that whenever a substance undergoes oxidation, it becomes electrically conductive.

The Examiner then proceeds to substitute every element but one (a viologen salt) of Sato's invention in order to arrive at the instant invention. Thus, a different substrate and grafting reagent are used for grafting benzyl chloride groups onto a substrate, for which Pohl is cited for the specific reagents used in the instant invention. Then, different reagents are used to form the viologen salt on the grafted substrate, for which Williams is cited. Finally, and most importantly, polyaniline is substituted for polyvinyl alcohol as the substrate polymer. Beratan is cited for this component. IBM Technical Disclosure Bulletin is cited as disclosing the formation of a viologen salt *in situ* upon a substrate, to address the deficiency of Williams in describing that a viologen salt should be formed other than in a homogeneous solution.

In the Office Action, the Examiner merely states a difference between the invention and what is described by Sato, then points to the missing element in one of the secondary references. No reasoning is provided as to why one of ordinary skill in the art would choose to make any substitution of Sato's composition, especially as to why polyaniline should be substituted for the PVA used by Sato. Thus, the Examiner is plainly indulging in improper hindsight reconstruction of the invention.

Furthermore, the Examiner has mischaracterized the Beratan reference. The Examiner states that Beratan discloses that polyaniline is a suitable electron donor for a viologen salt acceptor. Beratan does not make any conductive material comprising polyaniline. Beratan shows redox cycling between aniline and viologen monomer units in a polymer using a

ruthenium bipyridine intermediate. *See*, col. 6, lines 18-22. Such a composition is far afield from one comprising a viologen salt and polyaniline as distinct substances.

With respect to combining Sato with each and all of Pohl, Williams and Beratan, the Examiner states that substitution of one substance for another known to provide a similar function is obvious. However, the Examiner fails to explain why, from among all of the millions of possible chemical substances available to the skilled artisan to provide the various functional aspects of the claimed method, *i.e.* grafting sites, electron donation, etc., the particular substances disclosed by Pohl, Williams and Beratan should be used to make the (unmotivated) substitutions of Sato's composition. That is, the Examiner fails to show how the cited references provide "blazemarks" from the prior art method of Sato to the instantly claimed method, and thus fails to establish *prima facie* obviousness of the invention of claim 36. *See, In re Baird* 29 USPQ2d 1550 (Fed. Cir. 1994).

For all of the above reasons, the Examiner fails to establish a legally sufficient case of *prima facie* obviousness of the invention of claim 36. Accordingly, the present rejection of claim 36 under 35 USC § 103(a) is improper and must be withdrawn.

The present application well-describes and claims patentable subject matter. The favorable action of allowance of the pending claims and passage of the application to issue is respectfully requested.

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact Mark J. Nuell (Reg. No. 36,623) at

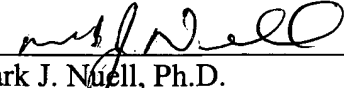
Application No. 09/895,153
Amendment dated October 13, 2005
Reply to Office Action of July 5, 2005

Docket No.: 1781-0233P

the telephone number of the undersigned below, to conduct an interview in an effort to expedite prosecution in connection with the present application.

Dated: October 13, 2005

Respectfully submitted,

By 
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Attachment: Ogawa et al. Reference (Radiat. Phys. Chem. Vol. 29, No. 5, pp. 353-357, 1987)

POLY(VINYL ALCOHOL) FILM CONTAINING METHYL VIOLOGEN AS A HIGHLY SENSITIVE DOSIMETER

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Abstract—Color development of polymer films containing methyl viologen (MV^{2+}) as an electron acceptor by gamma- or electron-beam irradiation was studied. The ionizing radiation induced one-electron reduction of MV^{2+} to produce the intensely blue-colored cation radical ($MV^{+•}$) in the polymer film. Poly(vinyl alcohol) (PVA) was an excellent matrix for the $MV^{+•}$ formation, leading to the greatest $G(MV^{+•})$ value of 9.8 among the polymers studied. The hydroxy groups of not only polymeric alcohol, PVA, but also monomeric alcohols added to poly(vinyl acetate) film were effective for promotion of the radiolytic one-electron reduction of MV^{2+} . The $G(MV^{+•})$ value obtained by gamma-irradiation of the MV^{2+} -PVA film was enhanced from 9.8 to 12.7 by the addition of sodium formate or potassium formate. The $MV^{+•}$ formed by ionizing radiation in the PVA matrix was extremely stable even when exposed to air. The MV^{2+} -PVA film is useful for a highly sensitive dosimeter in the lower dose range below 10 krad.

INTRODUCTION

Colorless methyl viologen (1,1'-dimethyl-4,4'-bipyridinium dication, MV^{2+}) undergoes one-electron reduction to the intensely blue-colored cation radical ($MV^{+•}$), as demonstrated in the thermo-, photo-, and electro-chemical reaction systems.⁽¹⁻⁵⁾ Pulse and steady-state radiolysis studies in aqueous solution have also shown the capturing of hydrated electrons by MV^{2+} to produce $MV^{+•}$.⁽⁹⁻¹²⁾ The blue color of $MV^{+•}$ disappears, due to regeneration of MV^{2+} , immediately when the $MV^{+•}$ is exposed to air in fluid media.^(13,14)

Recently we have studied the photoinduced electron-transfer reaction of methyl viologen salts, especially the dichloride ($MV^{2+}(Cl^-)_2$), in poly(vinyl alcohol) (PVA) film.⁽¹⁵⁾ Both PVA matrix and Cl^- counter ions were shown to act as electron donors to electronically excited MV^{2+} , thus producing stable cation radical $MV^{+•}$ even in the presence of air. The present study has focused on the formation of $MV^{+•}$ in PVA film by exposure to ionizing radiation such as γ -ray and electron beam. We describe herein how the PVA film containing MV^{2+} is applicable to a highly sensitive dosimeter.

EXPERIMENTAL

Methyl viologen dichloride ($MV^{2+}(Cl^-)_2$, >99% pure) was used as received from Aldrich Chemical. Poly(vinyl acetate) (PVAc, low molecular weight), 75% hydrolyzed PVAc (average molecular weight, $M_w = 3.0 \times 10^3$) and poly(vinyl alcohol) (PVA, $M_w = 1.4 \times 10^4$) were supplied by Aldrich Chemical. Hydrolyzed PVAc 87.5% ($M_w = 2.2 \times 10^4$), poly(N-

vinyl pyrrolidone) (PVP, $M_w = 3.6 \times 10^5$), and poly(acryl amide) (PAAm, $M_w = 7.1 \times 10^5$) were purchased from Nakarai Chemicals, and poly(acrylic acid) (PAA, 8×10^3 – 1.2×10^4 cps at 30°C) in ca 25 wt% aqueous solution from Wako Pure Chemical. All of the polymers were used without purification.

The polymer films containing MV^{2+} , other than PVAc, were prepared by cast-drying of aqueous mixture of the polymers and $MV^{2+}(Cl^-)_2$ on a glass plate for 48 h at room temperature and for another 24 h under reduced pressure of 20 mmHg immediately before irradiation. For preparing an MV^{2+} -PVAc film, methanol was used as solvent instead of water.

Irradiations were performed in N_2 or in air at room temperature with a ^{60}Co γ -ray at a dose rate of 23 krad/h or with 200-kV electron beam at a dose rate of 500 krad/s.

The irradiated films were analyzed at room temperature in air by a Shimadzu UV-200S spectrophotometer.

RESULTS AND DISCUSSION

Characteristics of one-electron reduction of MV^{2+} in PVA film by ionizing radiation

The PVA film containing $MV^{2+}(Cl^-)_2$ showed an absorption maximum at 263 nm due to MV^{2+} , being colorless and transparent.⁽¹⁵⁾ New absorption band maxima at 398 and 605 nm assigned to monomeric cation radical ($MV^{+•}$)^(13,14) appeared by exposure of the PVA film to γ -ray or electron beam, as illustrated typically in Fig. 1. Thus, the ionizing radiation induces one-electron reduction of MV^{2+} to the intensely blue-colored cation radical ($MV^{+•}$) in the

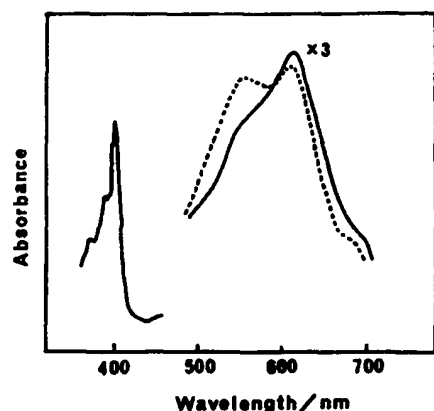


Fig. 1. Representative u.v. spectra of methyl viologen cation radicals: (—) monomeric $MV^{\bullet+}$; (---) a mixture of monomeric and dimeric $MV^{\bullet+}$. The spectra at wavelengths above 500 nm were illustrated with 3-fold magnified absorbance.

PVA film. Another new absorption maximum at 555 nm due to dimeric cation radical ($(MV^{\bullet+})_2$) formation^(15,16) was observed with increasing the radiation dose above *ca* 0.35 Mrad (Fig. 1).

Both monomeric and dimeric $MV^{\bullet+}$ were formed in the PVA film under conditions of higher-dose irradiation. In such a case, the total yield of cation radicals formed in PVA film ($(MV^{\bullet+})_t$) is given by the sum of monomeric (C_m) and dimeric (C_d) terms in mmol/g-PVA unit, as in equation (1).

$$[MV^{\bullet+}]_t = C_m + 2C_d \quad (1)$$

As reported elsewhere,⁽¹⁵⁾ the concentrations of monomeric $MV^{\bullet+}$ and dimeric $MV^{\bullet+}$ can be evaluated spectrometrically by the use of equations (2) and (3),

$$A_{605} = (1014 C_m + 2028 C_d) / l \quad (2)$$

$$A_{555} = (714 C_m + 3028 C_d) / l \quad (3)$$

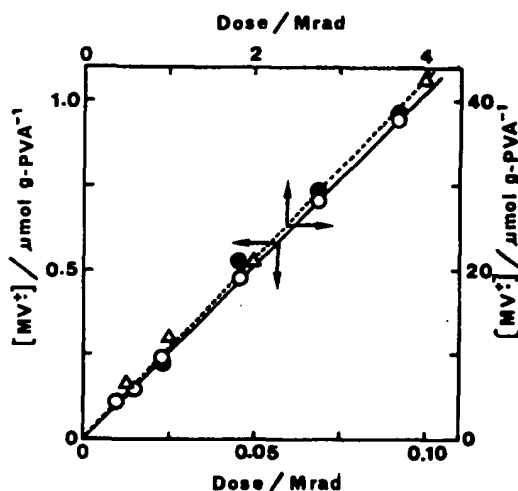


Fig. 2. Dose-yield plots for methyl viologen cation radical ($MV^{\bullet+}$) formed in poly(vinyl alcohol) film containing methyl viologen (MV^{2+} ; 0.1 mmol/g-PVA) on gamma-irradiation of 780- μ m films (○) in N_2 and (●) in air, and electron-beam irradiation of 40- μ m film (△) in N_2 .

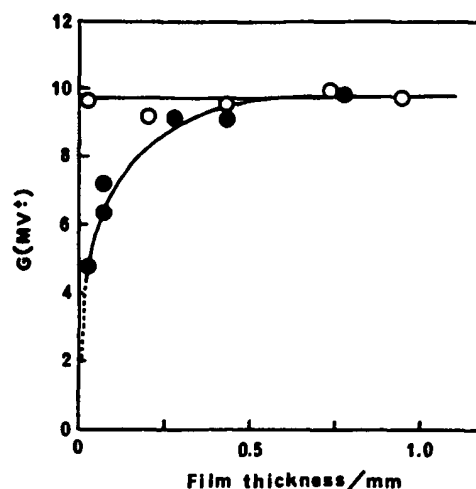


Fig. 3. Dependence of G value of methyl viologen cation radical ($G(MV^{\bullet+})$) on the thickness of poly(vinyl alcohol) film containing methyl viologen (MV^{2+} ; 0.1 mmol/g-PVA): gamma-irradiation (○) in N_2 and (●) in air.

where A_{605} and A_{555} are the absorbances at 605 and 555 nm, respectively, and l is the film thickness in mm unit.

The total yield of cation radicals, $(MV^{\bullet+})_t$, calculated for the gamma-irradiated PVA film (780 μ m thick) following the above procedure increased linearly with increasing the radiation dose (D), independent of the irradiation atmosphere whether in N_2 or in air (Fig. 2). From the slope of this linear plot, the G value for the $MV^{\bullet+}$ formation ($G(MV^{\bullet+})$) was obtained as 9.8 ± 0.6 . Figure 3 shows variation of the $G(MV^{\bullet+})$ values as a function of the MV^{2+} -PVA film thickness. In the case of gamma-irradiation in N_2 , the $G(MV^{\bullet+})$ value was almost independent of the film thickness. On the other hand, the $G(MV^{\bullet+})$ value in air decreased with decreasing the film thickness from 300 μ m, although it was little affected in the greater range of thickness from 300 to 1000 μ m. As discussed below, the behavior in air is attributable to partial quenching of $MV^{\bullet+}$ by O_2 (see also equation (15)) occurring in the near-surface region of the irradiated MV^{2+} -PVA film. It is also noted that the optimum initial concentration of $MV^{2+}(Cl^-)_2$ for obtaining higher $G(MV^{\bullet+})$ value ranged from 0.05 to 0.1 mmol/g-PVA. Thus, under the present conditions the ultimate $G(MV^{\bullet+})$ value was 9.8 using the MV^{2+} -PVA film.

For comparison, the MV^{2+} -PVA film (40 μ m thick) was exposed to 200-kV electron beam in N_2 . The depth-dose curve, which was measured for the 200-kV electrons with a plastic dosimeter of cellulose triacetate film, showed the maximum dose at *ca* 40 μ m depth. It is also indicated that the dose is almost constant (98–100% in relative value) for the MV^{2+} -PVA films with thickness below 100 μ m. As shown in Fig. 2, the dose-response of $(MV^{\bullet+})_t$ on the electron-beam irradiation was practically equivalent to the gamma-irradiation of 780- μ m film; $G(MV^{\bullet+})$

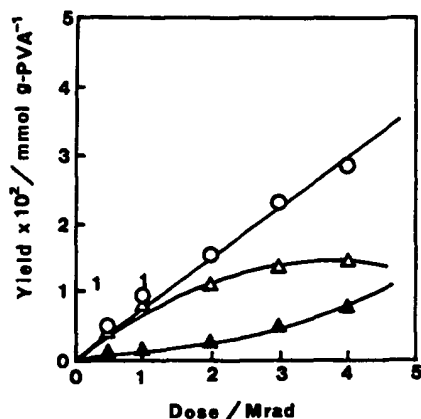
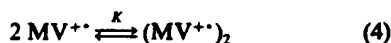


Fig. 4. Dose-yield plots of (O) total methyl viologen cation radical ($(MV^{2+})_t = C_m + 2C_d$), (Δ) monomeric MV^{2+} (C_m), and (\blacktriangle) dimeric MV^{2+} (C_d) on gamma-irradiation of poly(vinyl alcohol) film (70 μ m thick) containing methyl viologen (MV^{2+} ; 0.1 mmol/g-PVA) in air.

value was obtained as 10.4 ± 0.9 . Similarly, the electron-beam irradiation of 100- μ m film resulted in nearly equal $G(MV^{2+})$ value of 9.2.

In contrast to $(MV^{2+})_t$, the plots of C_m and C_d vs D gave upward-convex and concave curves, respectively (Fig. 4). The formation of dimeric MV^{2+} was negligibly small at radiation doses lower than ca 0.35 Mrad, while it was favored by the increasing total yield of cation radicals, $[MV^{2+}]$. These results show that the dimeric MV^{2+} is attributed to the enhanced association of monomeric MV^{2+} , as in equation (4).^(16,17)



The apparent association constant $K (= C_d/C_m^2)$ in the PVA film was evaluated as 34 g-PVA/mmol from the linear portion of Fig. 5. This K value (equivalent to $34 M^{-1}$ on assuming the density of PVA as 1 g/cm³) in the solid PVA matrix is one order of magni-

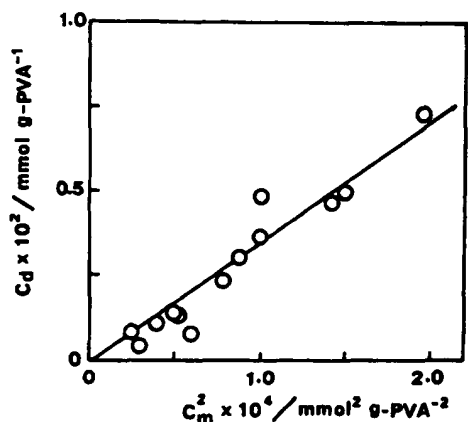


Fig. 5. Linear relationship between dimeric and monomeric methyl viologen cation radicals (MV^{2+}), C_d vs C_m^2 , formed on gamma-irradiation of poly(vinyl alcohol) film containing methyl viologen (MV^{2+} ; 0.1 mmol/g-PVA).

tude smaller than the reported value (ca 400 M^{-1})⁽¹⁶⁾ in solution. It is reasonable to expect that the association of monomeric MV^{2+} in the solid is significantly depressed due to the restricted mobility.

Effect of various polymer matrices on the radiolytic reduction of MV^{2+}

In order to clarify what type of polymer is the best matrix for the MV^{2+} formation by gamma-irradiation, we further evaluated the $G(MV^{2+})$ values in poly(vinyl acetate) (PVAc), poly(acrylic acid) (PAA), and poly(*N*-vinyl pyrrolidone) (PVP) films.

As listed in Table 1, the MV^{2+} formation could not be observed upon exposing MV^{2+} -PVAc film to γ -rays in N_2 . The $G(MV^{2+})$ value became greater with increasing the saponification value of PVAc, thus increasing the amounts of hydroxy groups of polymer matrix. The maximum $G(MV^{2+})$ value of 9.8 ± 0.6 was achieved using PVA (i.e. 100% hydrolyzed PVAc) matrix. These results suggest that the hydroxy groups of PVA play an important role in the radiolytic reduction of MV^{2+} to MV^{2+} .

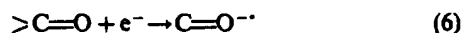
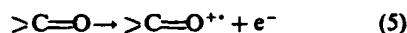
The $G(MV^{2+})$ values in PAA and PVP films were 0.3 and 4.6, respectively, and were smaller than in PVA film. Because of the failure to prepare a good film of poly(acryl amide) (PAAm) containing $MV^{2+}(Cl^-)_2$, we made a comparative experiment using a mixed polymer film of PAAm and PVA (1:1 weight ratio) (see Table 1). The $G(MV^{2+})$ value in the PAAm/PVA mixed film was 2.2, which was much smaller than in one-component PVA film. It is thus suggested that PAAm is a much less effective matrix for the radiolytic MV^{2+} formation. Among the polymers studied, except for PVA, PVP gave the greatest $G(MV^{2+})$ value, probably due to an N atom in the side-chain pyrrolidone group acting as a strong electron donor to MV^{2+} . It is apparent that the side-chain groups of the vinyl polymers play a crucial role as electron donors in the radiolytic reduction of MV^{2+} to MV^{2+} . PVA is the best polymer matrix for MV^{2+} formation. All the polymers such as PVP, PAA, PVAc and PAAm, which have electron accepting carbonyl ($>C=O$) groups in their side chains, decreased the $G(MV^{2+})$ value relative to PVA. It seems likely that the net electron-transfer ability of the side-chain $>C=O$ groups of these polymers toward MV^{2+} are much smaller than that of the hydroxy groups of PVA, as a result of either back

Table 1. G values of methyl viologen cation radical ($G(MV^{2+})$) formed in various polymer films containing methyl viologen (MV^{2+}) on gamma-irradiation in N_2 ^a

| Polymer film | $G(MV^{2+})$ |
|------------------------------------|---------------|
| Poly(vinyl acetate) | PVAc |
| 75.0% Hydrolyzed PVAc | 0 |
| 87.5% Hydrolyzed PVAc | 4.5 ± 0.2 |
| Poly(vinyl alcohol) | PVA |
| Poly(acrylic acid) | PAA |
| Poly(<i>N</i> -vinyl pyrrolidone) | PVP |
| PVA-Poly(acryl amide) | PVA-PAAm |
| | 9.8 ± 0.6 |
| | 0.3 ± 0.1 |
| | 4.6 ± 0.1 |
| | 2.2 ± 0.1 |

^a $[MV^{2+}] = 0.1$ mmol/g-polymer; polymer films were 780 μ m thick.

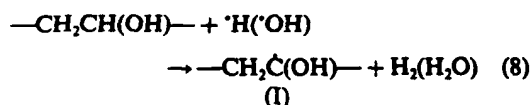
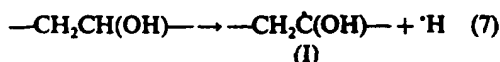
electron-transfer reaction (equation (5)) or electron-capture reaction [equation (6)].⁽¹⁹⁾



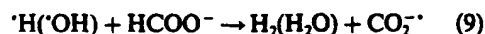
Effect of additives on the radiolytic reduction of MV^{2+} in polymer matrix

Addition of ethylene glycol to the nonsensitive PVAc film containing MV^{2+} gave rise to absorption at 605 nm due to $\text{MV}^{\cdot+}$ upon gamma-irradiation, while the effect of ethers was negligibly small (Table 2). This observation indicates that the hydroxy groups of not only polymeric alcohol, PVA, but also monomeric alcohols added to the inert PVAc matrix are effective for the radiolytic one-electron reduction of MV^{2+} to $\text{MV}^{\cdot+}$.

It is known that the radiolysis of alcohols generates several kinds of reducing species such as solvated electrons (e_{sol}^-), hydrogen atoms (H^\cdot) and alcohol-derived radicals ($\text{R}_1\text{R}_2\dot{\text{C}}\text{OH}$).⁽²⁰⁻²²⁾ Either e_{sol}^- or $\text{R}_1\text{R}_2\dot{\text{C}}\text{OH}$ is main species for the reduction of MV^{2+} .^(9,12) The formation of similar radicals, $-\text{CH}_2\dot{\text{C}}(\text{OH})-$, in the gamma-irradiated solid PVA has also been observed at room temperature by ESR measurement.⁽²³⁻²⁵⁾ In the present study, the G value for $\text{MV}^{\cdot+}$ formation in PVA film by gamma-irradiation was enhanced from 9.8 to 12.7, when sodium formate or potassium formate was added (Table 3). The role of the formate seems to be an efficient conversion of radicals to a reducing species of $\text{CO}_2^{\cdot-}$, which is reactive toward MV^{2+} .^(11,26) The increment of $G(\text{MV}^{\cdot+})$ in PVA film with excess amounts of formate was 2.9, which is comparable to the concentration of PVA-derived radicals ($G = 2.5$) determined by ESR at room temperature. Thus, the promotion effect of formate on the $\text{MV}^{\cdot+}$ formation may be related to the formation of PVA radicals (I), as in equations (7) and (8).^(27,28)



Reaction (9) may also occur in the presence of formate.



It is likely that the enhanced $G(\text{MV}^{\cdot+})$ value (the

Table 2. Effect of additives on radiolytic formation of methyl viologen cation radical ($\text{MV}^{\cdot+}$) in poly(vinyl acetate) film^a

| Additive | Absorbance at 605 nm |
|---------------------------------|----------------------|
| None | 0 |
| Ethylene glycol | 0.21 |
| Ethylene glycol monoethyl ether | 0.03 |
| Ethylene glycol diethyl ether | <0.01 |

^a $G(\text{MV}^{\cdot+}) = 0.1$ mmol/g-PVAc; (additive) = 10 mmol/g-PVAc; radiation dose = 1.15 Mrad.

Table 3. Promotion effect of formates on radiolytic formation of methyl viologen cation radical ($\text{MV}^{\cdot+}$) in poly(vinyl alcohol) film^a

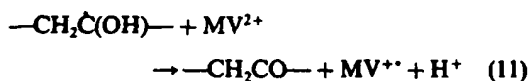
| Formate | $G(\text{MV}^{\cdot+})$ |
|-------------------|-------------------------|
| None | 9.8 ± 0.6 |
| Sodium formate | 12.8 ± 0.6 |
| Potassium formate | 12.6 ± 0.1 |

^a $G(\text{MV}^{\cdot+}) = 0.1$ mmol/g-PVA; (formate) = 1.0 mmol/g-PVA; PVA films were 780 μm thick.

increment of 2.9) in PVA film with formate is mainly due to the reduction of MV^{2+} by $\text{CO}_2^{\cdot-}$, as in equation (10).



It is known that $\text{R}_1\text{R}_2\dot{\text{C}}(\text{OH})$ radical has ability for one-electron reducing MV^{2+} .^(9,12) The corresponding PVA-derived radical may also be reactive toward MV^{2+} , as in equation (11).

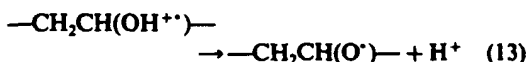


The $G(\text{MV}^{\cdot+})$ value due to reaction (11) is presumed to be smaller than the G value ($= 2.5$) for the $-\text{CH}_2\dot{\text{C}}(\text{OH})-$ radicals at room temperature.

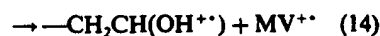
In view of the greater $G(\text{MV}^{\cdot+})$ value of 9.8 in PVA film, the radiolytic electron ejection (equation (12)) would be an important process for the reduction of MV^{2+} to $\text{MV}^{\cdot+}$.



The polymer cation radical thus produced is probably converted to the following type of polymer radical that may reduce MV^{2+} .^(3,29)



In addition, electronically excited PVA would account for the enhanced formation of $\text{MV}^{\cdot+}$ in PVA film.



Utility of $\text{MV}^{\cdot+}$ -PVA film in dosimetry

The linear relationship between $(\text{MV}^{\cdot+})_t$ and radiation dose, as in Fig. 4, shows that the MV^{2+} -PVA film is applicable to a dosimeter. Particularly, the MV^{2+} -PVA film is useful for the determination of lower doses of γ -ray below 10 krad, because both the absorbances at 398 and 605 nm due to monomeric $\text{MV}^{\cdot+}$ increased linearly with dose in its lower range; thus, the formation of dimeric cation radical $(\text{MV}^{\cdot+})_2$ is negligible. In this case, higher sensitivity may be obtained using the absorption of $\text{MV}^{\cdot+}$ at 398 nm because of the higher extinction coefficient. Several types of commercially available film dosimeters are commonly used for the determination of absorbed doses above 0.5 Mrad.^(30,31) In the comparative experiments, the sensitivity of the MV^{2+} -PVA film

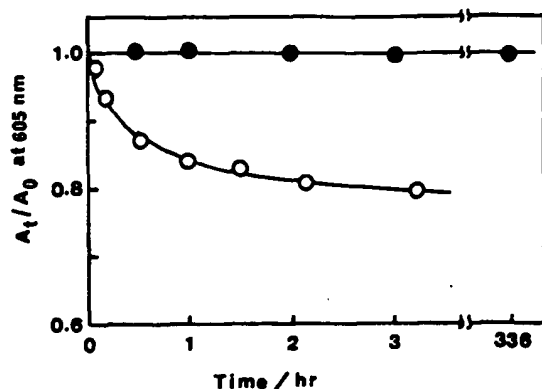
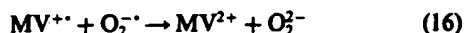
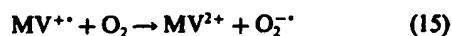


Fig. 6. Decay of methyl viologen cation radical (MV^{2+}) in poly(vinyl alcohol) films (O) without and (●) with polypropylene-poly(vinyl alcohol) laminate pack: A_0 , absorbance immediately after gamma-irradiation; A_t , absorbance at a given time after gamma-irradiation and exposure to air.

to γ -ray was *ca* 2500-fold greater than those of the commercially available dosimeters.

For practical use as a dosimeter, the stability of MV^{2+} in PVA film should be one of the important demands. In the previous study,⁽¹⁵⁾ fading of the characteristic blue color of MV^{2+} produced photochemically in the PVA matrix was observed when exposed to air. This behavior was interpreted in terms of one-electron oxidation of the MV^{2+} by O_2 to regenerate colorless MV^{2+} (equations (15) and (16)).



This fading was promoted when the PVA film was humified, probably due to the enhanced oxygen permeability with increased water content.⁽¹⁵⁾

Figure 6 shows the time decay in air of MV^{2+} formed in the gamma-irradiated PVA film. The decrease in the absorbance at 605 nm due to monomeric MV^{2+} was extremely slow, in contrast to prompt decreases in aqueous and alcoholic solutions upon exposure to air. Thus, the MV^{2+} formed in solid PVA matrix is unusually stable even in air.

In order to gain further stability of MV^{2+} in PVA film, the MV^{2+} -PVA film was packed *in vacuo* with thin laminate film composed of PVA and poly(propylene), before irradiation. The outer jacketed film could protect the MV^{2+} formed in the inner PVA film from air and water; the MV^{2+} was stable for at least 2 weeks in the presence of air, as shown in Fig. 6. In addition, using the vacuum-packed film, no decrease in the absorbance at 605 nm of monomeric MV^{2+} was observed for several hours even in water.

Further characterization of the MV^{2+} -PVA film for its application to dosimetry will be reported in a subsequent paper.

CONCLUSIONS

The present study has shown that MV^{2+} is subject to one-electron reduction to produce the intensely blue-colored MV^{2+} in solid PVA matrix by ionizing radiation such as γ -ray and electron beam. The MV^{2+} -PVA film is useful as a dosimeter for radiation doses lower than 10 krad.

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